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RESEARCH PAPER

Preparation and application of cationized pulp fiber as a papermaking wet-end additive

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Abstract: Cationized pulp fibers (CPF) were prepared by the adsorption of a novel biodegradable cationic ester quaternary ammonium salt (31441) on bleached softwood kraft pulp fibers. The optimized conditions for the CPF preparation were: 4% of 31441 (based on oven-dry pulp), 80°C and 30 min. The CPF was characterized by FT-IR, SEM and XPS. Experimental results showed that the CPF improved the retention of precipitated calcium carbonate (PCC) filler significantly. With 0.9% CPF (based on oven-dry pulp), the retention of PCC increased from 57.53% to 72.21%. The physical properties of paper were also slightly improved. The tensile strength and burst strength of the paper with CPF were higher than those with CPAM. CPF addition had no effect on the stock drainage.

Keywords: cationized pulp fiber; cationic ester quaternary ammonium salt; papermaking wet-end additive

Introduction

With the development and evolution of high-speed paper machines and more closed whitewater systems, the retention/drainage system become even more important in the papermaking process. Most papermaking wet-end additives are cationic polymers, some of which can be replaced by cationized pulp fibers (CPF) (Gruber 2002). The functioning mechanism of CPF on retention, drainage and reinforcement differs from those of conventional cationic additives. The mechanism of soluble cationic polyelectrolytes can be explained by the bridge trap theory (Ohno 1999). This bridge trap will only form a minor fraction of ion pairs. The size and force of the aggregates are very small and more influential. On the other hand, there are a large number of cations on the modified fiber surface, and they can form the three-dimensional net-like aggregates with fines and fillers. The size of the aggregates is very large and less influential. This is because these cationic charges have become a part of pulp fibers. Compared with conventional cationic aids, CPF is more effective in improving retention and drainage, neutralizing anionic trash, and reducing the white water load, as well as is also biodegradation (Halab-Kessira and Ricard 1999; Gruber and Granzow 1996, 1997; Sain and Boucher 2002).

As CPF is an advantageous papermaking wet-end additive, it has being attracted the attention of researchers of the pulp and paper industry both in China and in the world (Montplaisir et al. 2006a, b). If the technique of cationization can be improved, the cost of papermaking is likely to be decline, thus it may replace synthetic cationic aids. In this paper, CPF was prepared by the adsorption of a novel biodegradable cationic ester quaternary ammonium salt (31441, $[R\text{-}COOCH_2\text{-}N(CH_3)_2\text{-}CH_2COO\text{-}R]^+Cl^-$) on bleached softwood kraft pulp from Canada. The preparation conditions of CPF were optimized. CPF was characterized using FT-IR, SEM and XPS, and the application performance of CPF as a wet end additive was evaluated in this study.

Materials and methods

Materials

Bleached softwood kraft pulp was imported from Canada and wheat straw soda pulp was prepared in Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, China.. Cationic ester quaternary ammonium salt (abbreviation: 31441, content: 98%) was donated by Henan Titaning Chemical Technology Co., Ltd. (China), precipitated calcium carbonate (PCC, industry grade) was obtained from Guilin Wuhuan Industry Development Co., Ltd, and cationic polyacrylamide (CPAM) from Ciba Specialty Chemicals (China) Ltd.

Preparation of the Cationized Pulp Fibers (CPF)

First of all, a 1000-ml flask was placed in a constant temperature water bath, and 2 g (oven-dry basis) of pulp fiber was put into

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the flask. Then a certain amount of distilled water was added to the flask to adjust the pulp consistency to 2%. Next a predetermined amount of the 10 g/L solution of cationic ester quaternary ammonium salt (31441) was added using a transfer pipette. Finally, the mixture was stirred for a certain period of time at a certain speed to allow the 31441 to be adsorbed onto the pulp fiber. The pulp fiber absorbing the 31441 was filtered on a Büchner funnel with a piece of qualitative filter paper, and washed several times with distilled water.

Calculation of the adsorption percentage

The adsorption percentage (A) of the cationic ester quaternary ammonium salt (31441) adsorbed onto pulp fiber was calculated as follows:

$$A\ (\%) = (W_2 - W_1)/\ W_1 \times 100 \quad (1)$$

where W_1 is the oven-dry weight of pulp fiber before adsorption and W_2 is the oven-dry weight of pulp fiber after adsorption.

Evaluation of the retention and drainage

Two grams (oven-dry basis) of wheat straw soda pulp was mixed with 20% of PCC (i.e. 0.4 g) and a certain amount of CPF or 0.05% of CPAM (based on oven-dry pulp mass) to form a 1 000-mL suspension, and the beating degree (°SR) was measured to evaluate the drainage property of the filler-containing furnish. The turbidity of the filtrate obtained during the measurement of beating degree was measured to evaluate the retention property of PCC. The relationship between PCC concentration (C, %) and turbidity (T, NTU) was as follows:

$$T = 6401.7\ C - 7.5643 \quad (2)$$

The relationship between PCC retention (R) and PCC concentration (C) was as follows:

$$R\ (\%) = (0.4 - C \times 1000/100)/0.4 \times 100 \quad (3)$$

Measurement of the physical strength properties

Handsheets of 60 g/m^2 were prepared, with 20% of PCC (based on oven-dry pulp mass) as filler and 0.9% CPF or 0.05% CPAM (based on oven-dry pulp mass) as retention aids. Sample 1 was served as control sample with uncationized pulp fiber (UPF) instead of CPF. The tensile and burst strength of handsheets were measured according to the Chinese National Standard GB/T 453-2002 and GB/T 454-2002, respectively.

FT-IR, SEM and XPS analysis

Pellets of ca. 2 mg of samples were prepared by mixing with 200 mg of spectroscopic grade KBr. FT-IR spectra (4000–400 cm^{-1}) were recorded using a Nicolet MAGNA-IR 560 E.S.P. spectrometer.

SEM observation was performed using a FEI Quanta-200 environmental scanning electronic microscope. The specimens were treated by spray-gold before the observation and analysis. Prior to the XPS analysis, pulp sheets were made in a Büchner funnel and dried at room temperature. XPS spectra were obtained using a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer (XPS) system. An Al Kα X-ray source was used. The vacuum in the analyzing chamber was 1.0×10^{-8} Pa during analysis. The analyzer was operated at 50 eV pass energy for survey spectra. Elemental atomic concentrations were calculated from the XPS peak areas.

Results and discussions

Optimization of the CPF preparation conditions

Effect of the 31441 dosage

The adsorption of the 31441 onto pulp fiber increased with the increase of its dosage under the conditions of 80°C and 30 min. The adsorption percentage reached 2.89% when the 31441 dosage was 4%, and then leveled off (Fig. 1). Before the saturation adsorption, the amount of the 31441 adsorbed onto the pulp fibers increased as the dosage of the 31441 increased. However, as the dosage increased, the adsorption of the 31441 would reach a maximum when the available adsorption sites were exhausted. The optimum dosage of the 31441 was 4%.

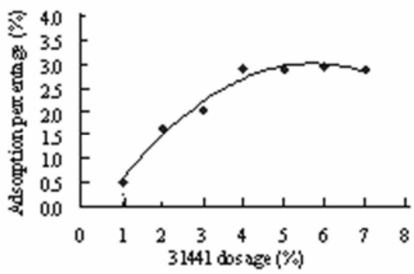

Fig. 1 Effect of the 31441 dosage on adsorption percentage. Conditions: T = 80°C, t = 30 min

Effect of temperature

The amount of the 31441 adsorbed onto pulp fibers increased with the increase of temperature under the condition of 4% the 31441, and 30 min. This was probably due to increased molecular activity of the 31441 and decreased medium viscosity at higher temperature. The adsorption at 20°C was higher than that at 40°C, probably due to inefficient washing of un-adsorbed 31441 from pulp fibers at low temperature.

Effect of time

The amount of the 31441 adsorbed onto pulp fibers increased with the reaction time. It reached a maximum percentage at about 30 min under the condition (4% the 31441, 80°C), then started to decrease. This may be explained by desorption and hydrolysis of the 31441 after the saturation point of adsorption. Therefore, the optimal adsorption time was 30 min under the conditions.

From the above discussion, the optimum preparation conditions of CPF were: 80°C, 4% the 31441 (based on oven-dry pulp), and 30 min. The CPF prepared under the optimum condi-

tions, was then used in the following experiments.

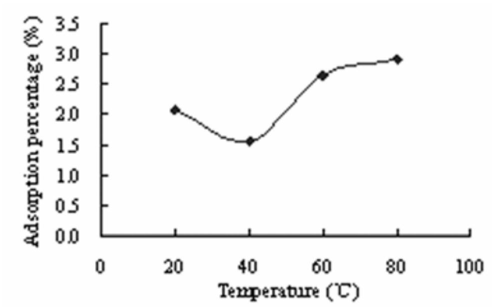

Fig. 2 Effect of temperature on adsorption percentage. Conditions: 4% 31441, 30 min.

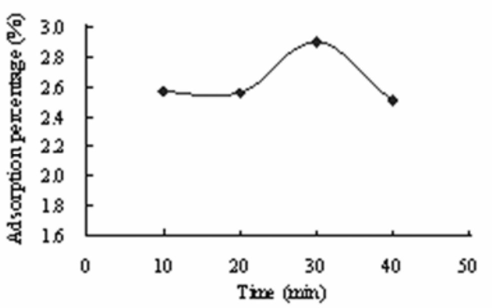

Fig. 3 Effect of time on adsorption percentage. Conditions: 4% the 31441, 80°C

Characterization of CPF

FT-IR analysis of CPF

Fourier transform infrared spectroscopic (FT-IR) analysis was performed in order to confirm the existence of the 31441 on the surfaces of CPF. The spectra were shown as Fig. 4. Compared to the spectrum of UPF, an additional absorption band at 1734 cm^{-1} was observed in the spectrum of CPF, although its intensity was weak due to low concentration of the 31441 in pulp fibers. This additional peak was attributed to the ester carbonyl group of the 31441.

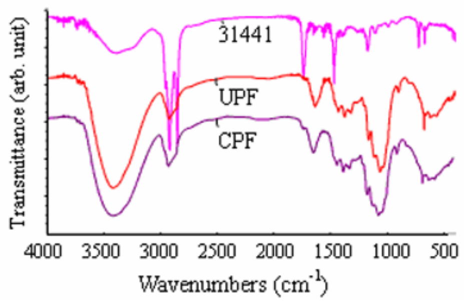

Fig. 4 FT-IR spectra of 31441, CPF and UPF. The adsorption percentage of 31441 onto CPF was 2.89%

SEM observation of CPF

In order to reveal the surface morphologies of pulp fibers before and after modification by cationic ester quaternary ammonium salt (31441), both the cationized pulp fibers and the uncationized pulp fibers were examined by SEM. The SEM images in Fig. 5 showed that the surface of CPF was smoother than that of UPF, probably due to the coverage of the 31441.

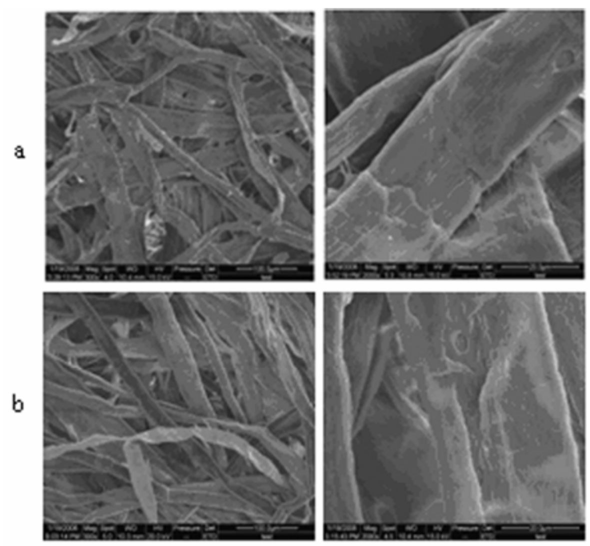

Fig. 5 SEM images of UPF (a) and CPF (b). The adsorption percentage of 31441 onto CPF was 2.89%

XPS analysis of CPF

As shown in Table 1, both nitrogen and chlorine elements were found in CPF but not in UPF, indicating the presence of 31441 on CPF.

Table 1. Elemental atomic concentrations of UPF and CPF. The adsorption percentage of 31441 onto CPF was 2.89 %.

Element	Peak position (eV)	CPF (*At* %)	UPF (*At* %)
C1s	284.60	76.2	59.17
O1s	532.27	22.66	40.83
N1s	402.12	0.67	--
Cl2p	197.15	0.46	--

Application of CPF in papermaking process

PCC retention improvement

The retention of PCC increased with the increase of CPF dosage while the turbidity of the filtrate decreased (Fig. 7). The PCC retention reached a maximum percentage of 72.21% when 0.9% of CPF was added. In comparison, the PCC retention was only 58.28% when 0.05% CPAM was added as the retention aid. However, a too high dosage of CPF (>1%) decreased PCC retention and increased the turbidity of the filtrate due to excessive amount of cationic charges from the CPF. The drainage of the stock was not affected by the addition of CPF.

Improvement of paper strength

Experimental results also showed that the CPF improved the strength properties when it was used to replace CPAM. For example, the tensile increased from 30.09 to 34.36 $kN \cdot m^{-1}$ and the burst from 142 to 158 kPa, when 0.05% CPAM was replaced

with 0.9% CPF.

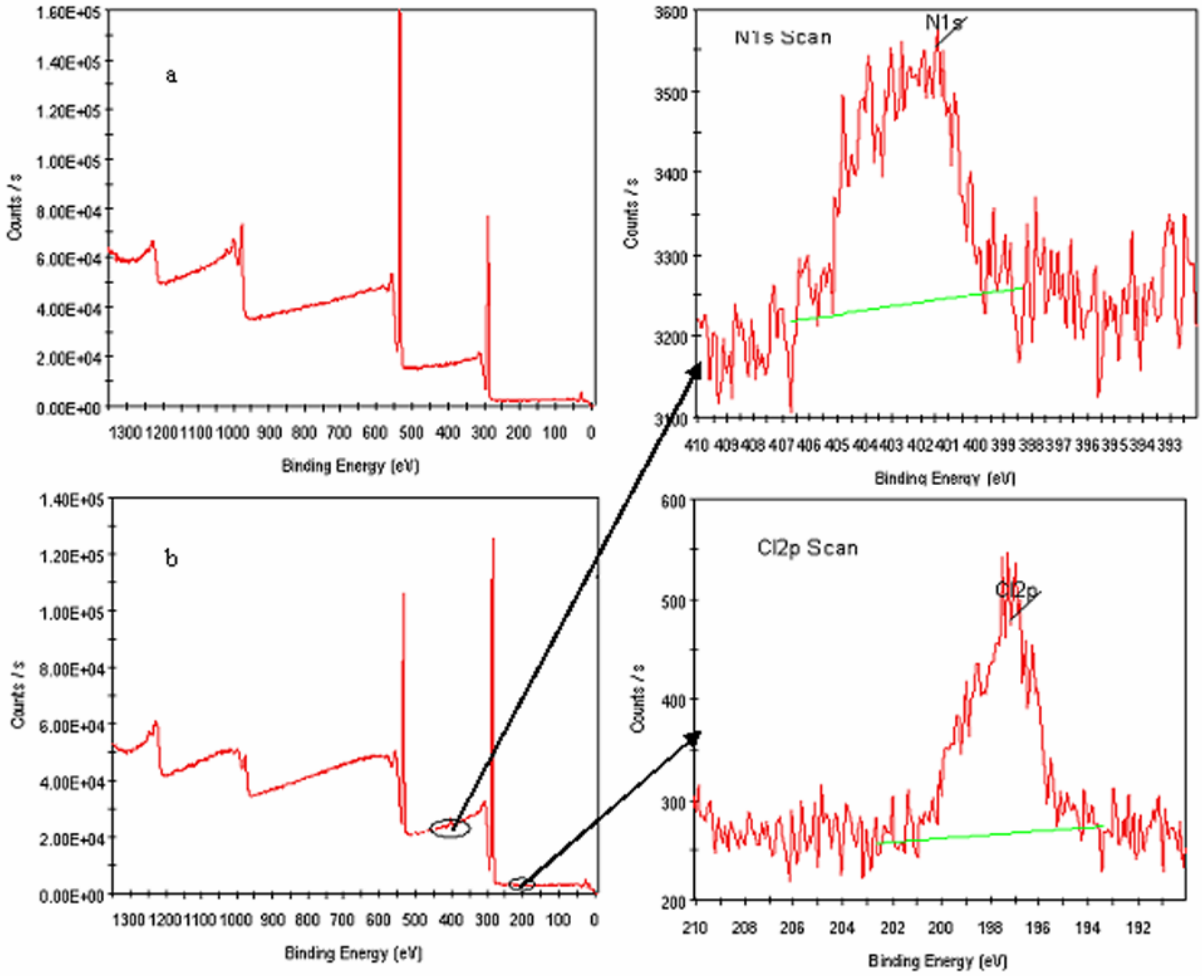

Fig. 6 XPS survey spectra of UPF (a) and CPF (b). The adsorption percentage of 31441 onto CPF was 2.89%.

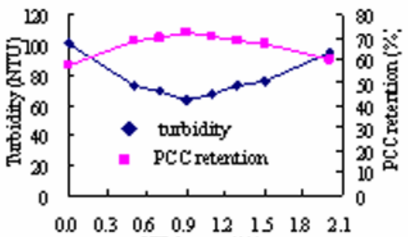

Fig.7 Improvement of CPF on PCC retention. The adsorption percentage of 31441 onto CPF was 2.89%.

Conclusions

A process was developed for preparing a cationic pulp. The optimized conditions for preparation of cationized pulp fibers (CPF) were: 80°C, 4% of the 31441 (based on oven-dry pulp), 30 min. The CPF could improve the retention of precipitated calcium carbonate (PCC) filler significantly: the PCC retention increased from 57.53% to 72.21% with the addition of 0.9% CPF (based on oven-dry pulp). The strength properties of paper were also slightly improved. CPF had no effect on the stock drainage.

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